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Differential Capacitance of Ionic Liquid Interface with Graphene: The Effects of Correlation and Finite Size of Ions

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August 19, 2019

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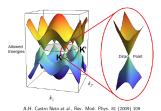
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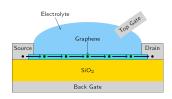
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Graphene:

- High mobility of charge carriers in π electron bonds
- Zero-Energy band gap
- Dirac cone approximation
- Operate as field effective transistors

π Electron Energy Over Brillouin Zone





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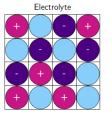
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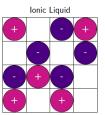
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Ionic Liquids





- Melting points below 100 C
- Comprised strictly of positive and negative ions
- High conductivity and lower volatility than typical electrolytes
- Inter ionic correlations and overscreening

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Free energy functional

Gibbs Free Energy:

$$F = U - TS$$

Functional for ionic liquids:

$$F = \int igg[-rac{arepsilon}{8\pi} (|
abla \phi|^2 + l_c^2 (
abla^2 \phi)^2) +
ho \phi - TS igg] d^3 r \, .$$

where the charge density ρ is defined as:

$$\rho = e(z_+c_+ - z_-c_-)$$

with the entropic term:

$$egin{aligned} -\,TS &= rac{K_BT}{v}[vc_-\ln\left(vc_
ight) + vc_+\ln\left(vc_+
ight) \ &+ \left(1-vc_--vc_+
ight)\ln\left(1-vc_--vc_+
ight)] \end{aligned}$$

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Poisson Fermi equation

Minimization w.r.t the concentration yields:

$$c_{\pm} = rac{c_{\infty}e^{eta\phi}}{1-\gamma+\gamma\cosh\left(zeeta\phi
ight)}$$

where c_∞ is the concentration in the neutral bulk, $\beta=rac{1}{K_BT}$ and $\gamma=2vc_\infty$ defines the ionic packing fraction

Minimization w.r.t the potential yields:

$$(1-\delta_c^2
abla^2)
abla^2\phi=-4\pi
ho$$

with $\delta_c=\frac{l_c}{\lambda_D}$ is a dimensionless correlation length with λ_D defining the Debye length in the ionic liquid

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Differential Capacitance in the Diffuse Layer

Charge density per unit area:

$$\sigma_d(\phi_0) = \int_0^\infty
ho(\phi(x);\phi_0) dx$$

Apply external voltage to the bulk resulting in a potential drop across the diffuse layer:

$$V_d = -\phi_0$$

Differential capacitance per unit area:

$$C_d = rac{d\sigma_d}{dV_d}$$

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1D Problem

• Exploit the planar geometry to solve a 1D the modified Poisson Boltzmann equation:

$$\phi^{''}-\delta_c^2\phi^{''''}=-4\pi
ho(\phi)$$

which the BCs:

$$\phi(0) = \phi_0, \phi(0)^{'''} = 0, \phi^{'}(\infty) = 0, \phi^{'''}(\infty) = 0$$

- Inclusion of Graphene requires non trivial changes to the Boundary conditions.
- Utilize the charge neutrality condition.

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Graphene electrode

Density of States:

$$D(arepsilon) = \iint rac{g}{(2\pi)^2} \delta(arepsilon - arepsilon(ec{k})) d^2ec{k}$$

which can be linearized by the Dirac Cone approximation to give:

$$D(arepsilon)pprox rac{2|arepsilon|}{\pi(\hbar v_F)^2}$$

Charge Density on Graphene:

$$\sigma_g(arepsilon_F) = -e\int D(arepsilon) iggl[rac{1}{1+e^{eta(arepsilon-arepsilon_F)}} - rac{1}{1+e^{etaarepsilon}} iggr] darepsilon$$

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Conclusions and Future Work Then we define the differential capacitance per unit area i.e the quantum capacitance as:

$${C}_g = -erac{d\sigma_g}{darepsilon_F}$$

which gives the following expression for C_g :

$$C_g = 2\Gamma_g \ln[2\coshrac{eta e V_g}{2}]$$

where
$$\Gamma_g=rac{2lpha^2}{\pi e^2eta}$$
, with $lpha=rac{e^2}{\hbar v_F}$, $v_Fpprox 10^6 m/s$ and $V_g=\mu_c/e$

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The Neutrality Condition

Applied potential:

$$V_a = V_d + V_g$$

Charge neutrality condition:

$$\sigma_d(V_d) + \sigma_g(V_g) = 0$$

Therefore, we can impose the charge neutrality condition to find the relationship between V_d and V_g to find the total capacitance $C_{dg} = \frac{d\sigma_d}{dV_a}$ as:

$$C_{dg} = [C_d(V_d)^{-1} + C_g(V_g)^{-1}]^{-1}$$

Differential

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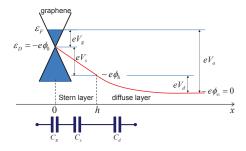
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Inclusion of a Stern Layer



$$V_s=rac{\sigma_d}{C_s}$$
 $C_s=\epsilon_s/(4\pi h)$ $C_{dsg}=[C_d(V_d)^{-1}+C_s^{-1}+C_g(V_g)^{-1}]^{-1}$

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Computational approach: Algorithm

- Solve the modified Poisson Fermi equation for an array of initial potential values ϕ_0
- For each ϕ_0 value we find $ho(\phi(x);\phi_0)$
- Numerically integrate to obtain $\sigma_d(\phi_0) = \int
 ho dx$
- Define $V_d \equiv -\phi_0$ and interpolate the set of V_d and σ_d values to obtain a numerical approximation of $\sigma_d(V_d)$
- Impose the charge neutrality condition $\sigma_d(V_d) + \sigma_g(V_g) = 0$ and solve for $V_d(V_a)$ and $V_g(V_a)$, using $V_a = V_d + V_s + V_g$
- Calculate C_d , C_s , C_g and C_{dsg} using the expressions derived for the capacitances.

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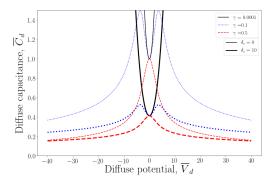
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Diffuse Layer Capacitance C_d



- Bell and camel shaped capacitances
- Ion correlations reduce the capacitance
- Independence of \overline{C}_d from δ_c for large γ at large $|\overline{V}_d|$

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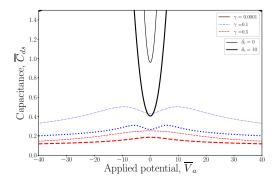
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Double Layer capacitance C_{ds}



Inclusion of Stern Layer lowers and broadens the capacitance peaks

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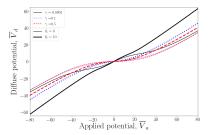
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Fraction of the total applied potential in diffuse layer, $V_a = V_d + V_a$



- Most of \overline{V}_a goes to \overline{V}_g i.e charging the graphene electrode
- $|\overline{V}_d|$ decreases with increasing γ and lowering δ_c
- ion correlations makes the differences for \overline{V}_d for different γ more pronounced.

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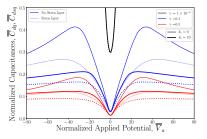
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Total Capacitances, C_{dg} and C_{dsg}



- \overline{C}_g dominating the total capacitance around the PZC
- Broad peaks and camel shaped dependence for $|\overline{V}_a| >> 10$ for both $\gamma = 0.1$ and 0.5
- Stern Layer and ion correlations broaden the overall capacitance

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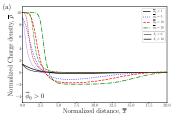
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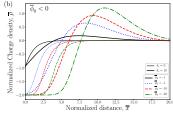
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Asymmetric Ionic Liquid: Charge density





- $\gamma_{+} = 0.5$ and $\gamma_{-} = 0.1$
- Ion crowding effects $\overline{
 ho}=rac{1}{\gamma_{\pm}}$ and saturation for large $\overline{\phi}_0$
- interplay of screening and overcrowding effects for large $\overline{\phi}_0$

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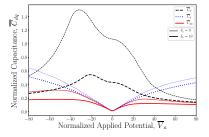
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Asymmetric Ionic Liquid: Capacitances



- Asymmetry in \overline{C}_d
- \overline{C}_q dominating around the PZC, V-shaped capacitance
- For $|\overline{V}_a| >$ 10, asymmetric camel shaped \overline{C}_{dq}

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Concluding Remarks

- Ion packing fractions $\gamma=0.1$ and $\gamma=0.5$ give rise to camel and bell-shaped diffuse capacitances C_d respectively
- Inclusion of Stern layer reduces and broadens the peaks in capacitances
- Quantum capacitance C_g dominates around the PZC giving rise to camel shaped capacitances
- Asymmetric ionic liquids have asymmetric camel shaped capacitances as well due to C_g

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- Fully asymmetric ionic liquid electrolytes
 - Different valency
 - Different Correlation Lengths
- Explore New Boundary Conditions

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Asymmetric Ionic Liquids

Consider the case for an asymmetric ionic liquid with equal valency $z_-=z_+=z$ but unequal ionic volumes v_-,v_+

$$egin{aligned} c_+ &= c_\infty rac{e^{-zeeta\phi}}{g(\phi)} \ c_- &= c_\infty rac{e^{-zeeta\phi}f(\phi)}{g(\phi)} \end{aligned}$$

where $f(\phi)$ and $g(\phi)$ are given by:

$$f(\phi)=\left(1+rac{zv_{-}c_{\infty}}{1-zv_{-}c_{\infty}(e^{zeeta\phi}-1)}
ight)^{rac{v_{+}}{v_{-}}-1}$$

$$g(\phi) = f(\phi) + z v_+ c_\infty [e^{-zeeta\phi} - f(\phi)] + z v_- c_\infty f(\phi) (e^{ezeta\phi} - 1)$$